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EFFECT OF ACIDIC CONDITIONS ON INTERFACE AND STRENGTH OF CELLULOSE FIBRES

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ABSTRACT

Composites were made with furan as matrix and aligned hemp fibres as reinforcement to obtain a completely biodegradable material. Since it is a new matrix material it is important to characterize the interface between fibres and matrix and the fibre strength. The resulting composites had reasonable stiffness (12-20 GPa) corresponding to a fibre stiffness of 62 GPa. The images showed a good impregnation of the fibre bundle surface. The fracture surface was perpendicular to the fibre axis indicating a relatively strong interface. Separate experiments on fibre bundles under acidic conditions indicate that the strength of the fibres suffers severe reduction at pH below 2.

1. INTRODUCTION

In order to make composite materials reinforced with cellulose based fibres from hemp and flax it is important that a good interface is established and that the fibres are not degraded in the process. The process conditions may affect both the surface and the bulk of the fibres, leading to potential changes (reductions) in respectively fibre-matrix interface binding and in fibre strength and stiffness. A reduction in interface binding efficiency leads to lower composite strength and stiffness, and a reduction in fibre strength and stiffness leads to a general reduction in composite mechanical properties. It is therefore important to determine process conditions (e. g. pH-level) that the fibres can tolerate without severe degradation.

Composites were made with aligned hemp yarn in furan matrix at various fibre contents. These composites were tensile tested to determine the composite and fibre properties. Light microscopy was used to observe the impregnation of the fibres, and the composite fracture surfaces were used to determine composite failure mechanism. Fibre bundle tests were performed to determine the effect of pH level on the resulting fibre strength. Chemical analysis

was used to see if some components in the fibres were degraded.

2. MATERIALS AND METHODS

2.1. Treatment of hemp fibres at varied pH levels. Fibre sliver produced by alignment of hemp fibres was mixed with water at varied pH levels in the range pH = 1-7. The suspensions with fibres were incubated for 1 h at 30ºC, 1 h at 50ºC and finally 1 h at 80ºC. The fibres were dried overnight at 60ºC. The treated fibres were tested in fibre bundle tests and analysed for chemical composition.

2.2. Fibre bundle strength. Fibre bundles were tested at 23°C and 50% relative humidity. Tensile tests on fibre bundles (15 mm long l_f) were done with a 3 mm test span l_{span} at a strain rate of 3.4×10^{-4} s^{-1} (0.06 mm/min) using an Instron 5566 with pressley clamps [Type: Stelometer 654 from Zellweger Uster]. After fracture the fibre pieces of 15 mm were weighed w_f. The failure stress σ_{fu} was calculated based on the failure force F_{fu} and the fibre density ρ_f, which was 1.58 g/cm^3 for the investigated hemp fibres:

$$\sigma_{fu} = \frac{F_{fu}}{A_f} = F_{fu} \times \frac{l_f \times \rho_f}{w_f}$$

2.3 Chemical fibre analysis. The chemical composition of the fibre samples was determined using a gravimetric method (Browning, 1967; Thygesen et al., 2005). Fibres were initially milled in a knife mill and passed through a 1 mm sieve. Consecutively, degradation and extraction of wax, water-soluble components, pectin, lignin, and hemicellulose in the milled fibres was performed in the chemical analysis. The residual part was almost pure cellulose with a low content of minerals, estimated by ash determination.

2.4. Fabrication of furan-hemp fibre laminates. Aligned fibre assemblies were made from filament-winding of hemp yarn (47 tex). The hemp yarn has previously been studied for reinforcement of thermoplastics (Madsen, 2004). The fibre assembly was manually impregnated with two-component furan resin. A roller was used to distribute the furan uniformly within the fibre assembly. The furan impregnated fibre assembly was pressed to a fixed thickness (= 4 mm) between two press plates by using clamps. Prior to fabrication, the press plates were treated with a release agent (Zyvax Multishield). The curing of the composite laminate started at 30ºC for 3 h, then at 60ºC for 1.5 h and finally at 80ºC for 1.5 h. After removal from the mould the laminates were post cured at 80ºC for 18h and 110ºC for 3 h. Laminate dimensions were approx. 300×220 mm^2. The three levels of tested fibre volume fraction were 15 %, 25 % and 35 %.

3. RESULTS AND DISCUSSION

3.1. Results of the composite tests regarding mechanical properties. The tensile test of the laminates was performed in the fibre direction. The resulting stress-strain curve is shown in Figure 1. The calculated composite stiffness is shown in Figure 2.

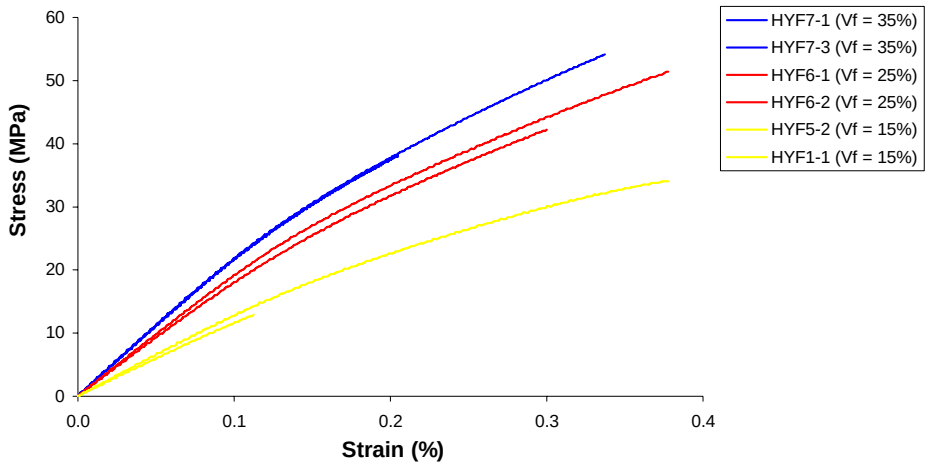

Figure 1. Tensile stress-strain curves of the fabricated aligned hemp fibre/furan composites with variable fibre volume fractions.

The results in Figure 1 show that the overall shape of the curves is the same for all composites irrespectively of their fibre content. The curves consist of an initial linear stress-strain relationship until a yielding point, which is followed by non-linear stress-strain relationship until failure.

The stress-strain performance of the composites is influenced by the content of fibres; the curves are clearly grouped according to the three levels of fibre volume fractions. The curves are shifted in an upward direction when the fibre content is increased, which means that stiffness and strength are increased correspondingly. The yielding point of the curves seems also to be increased with the fibre content. The failure strains were similar at the three levels of fibre content.

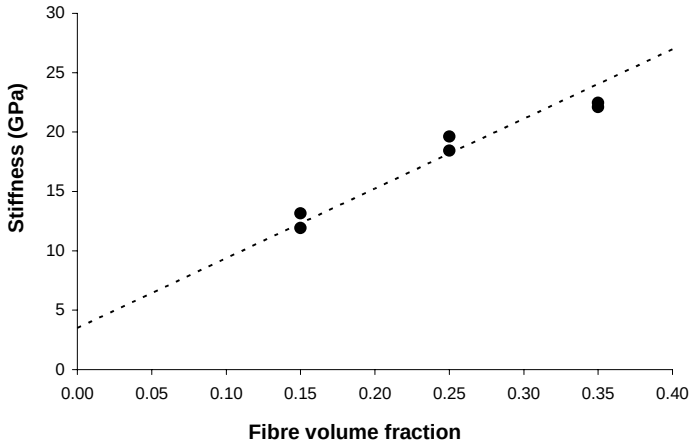

Figure 2. Stiffness of aligned hemp fibre/furan composites as a function of fibre volume fraction. Dotted line is model predictions.

The prediction line in Figure 2 is calculated by the rules-of-mixtures model traditionally used for unidirectional fibre composites. Previously, the stiffness of neat furan samples has been measured to be about 3.5 GPa (unpublished data), and this has been used in the model

calculations (at $V_f = 0$). The model predictions were fitted to the experimental data leading to an effective fibre stiffness of 62 GPa. The results in Figure 2 show also that stiffness of the composites is increased linearly as a function of the fibre volume fraction, which is as expected according to the model predictions. Thus, in terms of stiffness, the aligned hemp fibre/furan composites behave as normal composite materials.

The determined fibre stiffness of about 60 GPa has previously been found in a study of composites with the same type of fibres, but with other types of matrices like epoxy and PET (Madsen, 2004;Thygesen et al., 2007). The interface between fibres and matrix thereby seems to be as good for furan as for PET-resin and epoxy resin.

3.2. Results of the composite tests regarding micro structural properties. Two cross-sectional images of a furan matrix composite with aligned hemp yarn fibres are shown in Figure 3. The images are obtained by optical microscopy: (left) is high-magnification, and (right) is low-magnification.

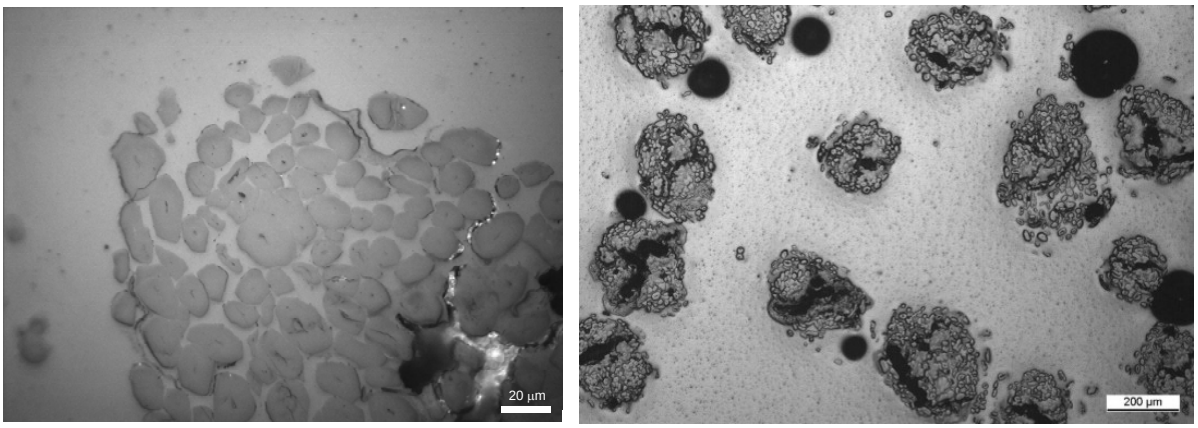

Figure 3. Cross sectional images of the hemp fibre composites with 15 volume-% fibres obtained by optical microscopy: (left) is high-magnification, and (right) is low-magnification.

The images demonstrate that the hemp yarn bundles are not perfectly impregnated with the furan resulting in porosities (i.e. black areas) located inside some of the bundles. Thus, future work must be focused at improvements of the fibre impregnation: e.g. by lowering the viscosity of the furan, and/or by increasing the available time for fibre impregnation before curing of the furan. However, the fibre impregnation may very well also be improved by using another composite fabrication method than compression moulding e.g. vacuum infusion. The compatibility between furan and hemp fibres seems to be good, since there are no (or only few) apparent interfacial gaps. This can be observed in the high-magnification image (left).

The test specimens after failure are shown in Figure 4. The fracture seems to occur along an almost straight line perpendicular to the fibre direction. This indicates that the interface is strong since fibres otherwise would be pulled out of the matrix resulting in a broad failure zone as observed with untreated fibres (Madsen, 2004). These fibres were roughly 7 times stronger so a stronger interface and better fibre impregnation were required.

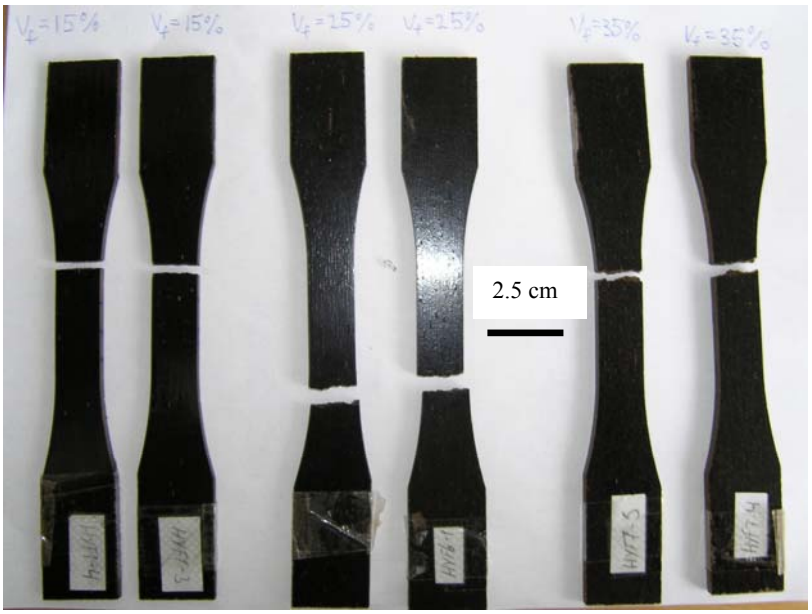

Figure 4. Tensile test specimens with varied fibre content and the furan matrix. The volume fraction of fibres were 15%, 25% and 35%, respectively.

3.3. Effect of the acidic conditions on the fibres. The effect of pH was tested since hydrolysis of cellulose and hemicellulose can occur at acidic conditions (Figure 5). Degraded bindings within the fibres are expected to reduce the fibre strength.

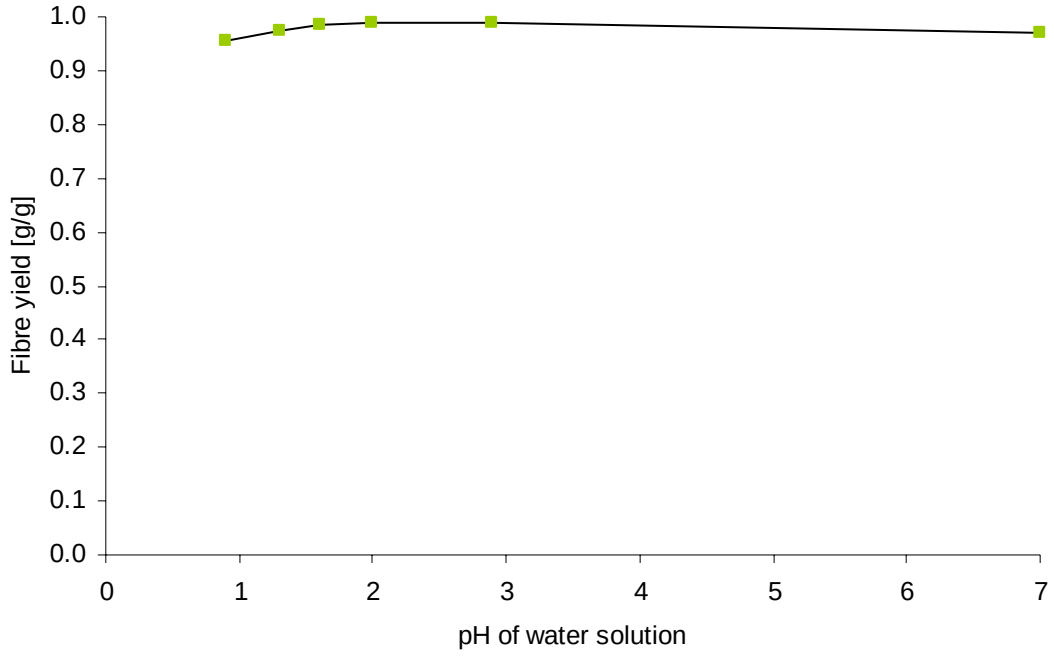

Figure 5. Effect of pH on fibre yield.

The yield of fibres was high during all treatments. The extraction of material is thereby low at these conditions. The chemical composition of the fibres after the treatments is shown in Table 1. The cellulose fraction in the fibres was not changed in the treatment. However since the fibre yield was 97-99 g/100 g raw fibres a small amount of cellulose was extracted (0-2 g/100 g

raw fibres). The other compounds that were partly extracted were lignin (2 g/100 g raw fibres), wax (2 g/100 g raw fibres) and ash (1-2 g/100 g raw fibres). Increases in contents were observed for hemicellulose (1-3 g/100 g raw fibres) and pectin (0-2 g/100 g raw fibres). The composition of the fibres is thereby slightly modified in the treatment and the hemicellulose remained solid even though low pH was used. The decrease in fibre strength is therefore probably due to acidic damage of cellulose chains and other chemical bindings in the fibres.

Table 1. Chemical composition of the hemp sliver after treatment at the varied pH levels.

Treatment hemp sliver	Cellulose %(w/w)	Hemicel. %(w/w)	Lignin %(w/w)	Pectin %(w/w)	Water ext. %(w/w)	Wax %(w/w)	Ash %(w/w)
Raw sample	**73.4**	**14.6**	**4.3**	**2.4**	**0.0**	**3.2**	**2.1**
pH = 7.0	74.1	16.3	2.6	3.7	2.9	0.0	1.4
pH = 2.0	75.3	15.1	2.6	2.9	2.2	1.1	0.8
pH = 1.6	73.7	16.4	2.8	2.5	2.8	1.5	0.4
pH = 1.3	73.0	17.4	2.6	4.2	1.2	1.2	0.3
pH = 0.9	73.6	17.4	2.0	4.5	1.3	0.9	0.4
Standard deviation	0.6	0.2	0.2	0.3	0.4	0.6	0.1

Fibre bundle stress-strain curves of the hemp fibres treated at different pH-values are shown in Figure 6. The slope of the curves for stress versus strain is highest when the fibres had been treated at high pH-values leading to high fibre stiffness and fibre strength. The fibres become weaker due to acidic hydrolysis at the low pH-level (0.9-1.2).

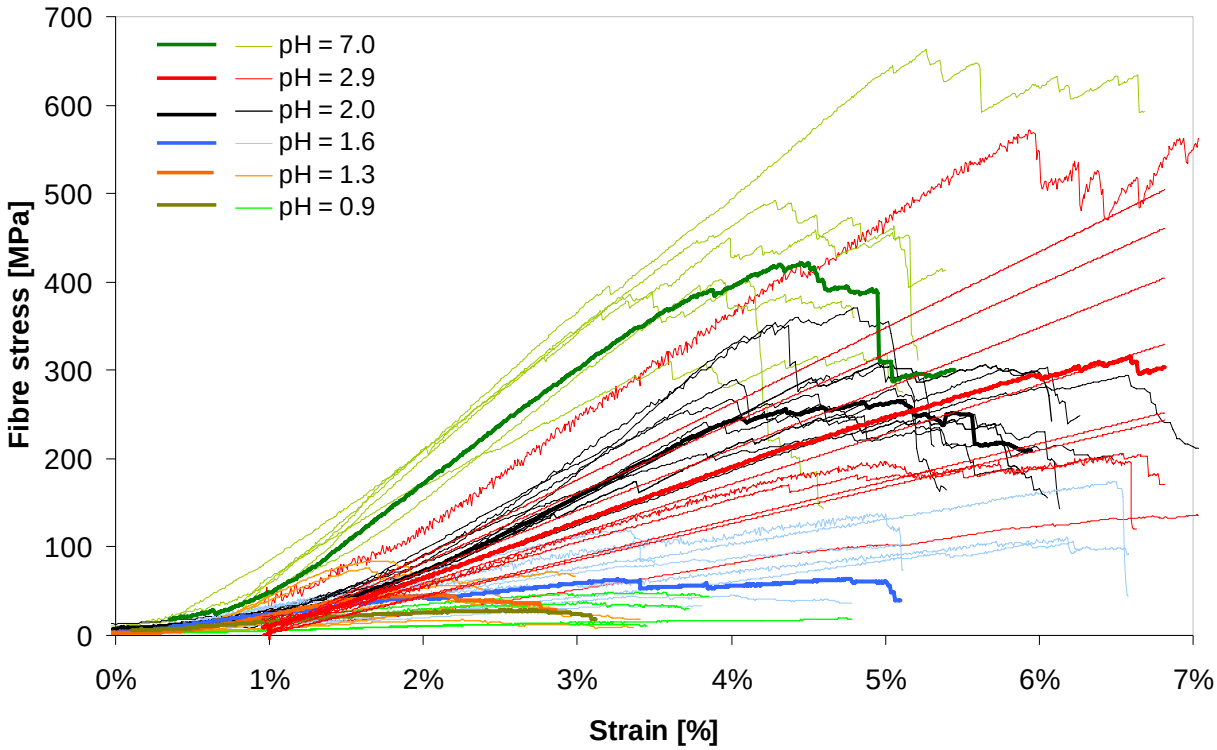

Figure 6. Fibre bundle tests on hemp sliver treated at different pH-values. The individual curves are shown (thin lines) and the average curves are shown (thick and darker lines).

Fibre bundle strength of the hemp fibres treated at variable pH-values is shown in Figure 7. Taking the large variability of the measurements into account, the strength seems to be in the

range 300-500 MPa at high pH-values. At lower pH-values, the fibre bundle strength is clearly decreased: the rate of acidic hydrolysis resulting in chemical fibre damage is thereby increasing versus decreasing pH.

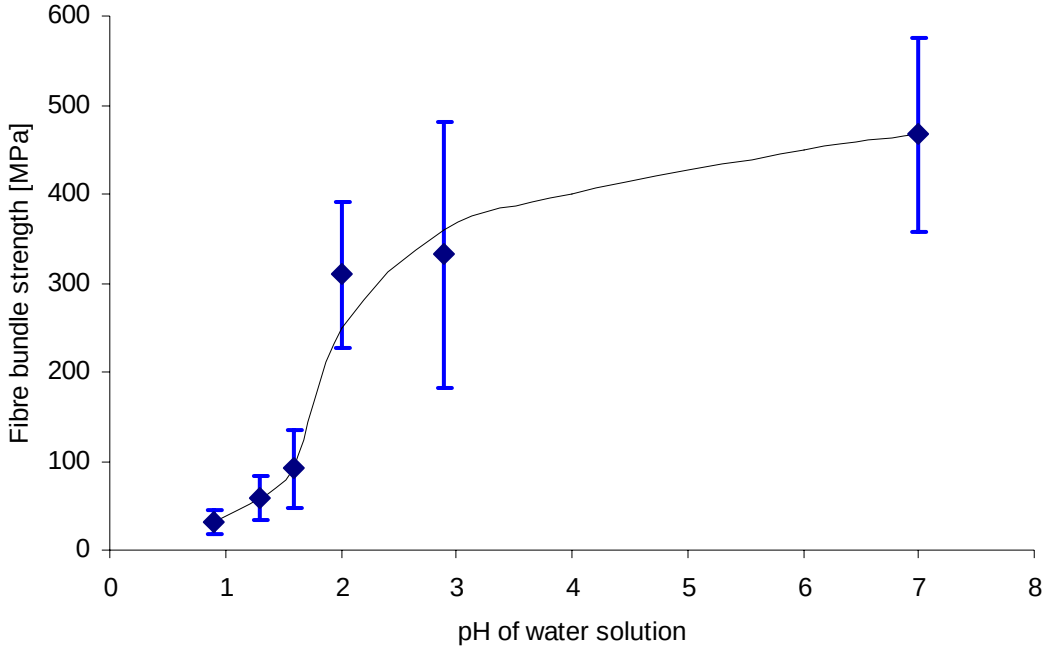

Figure 7. Fibre strength obtained versus pH of the water solution

4. CONCLUSION

The resulting composites have reasonable stiffness corresponding to a fibre stiffness of 60 GPa.

The images show a good impregnation of the fibre bundle surface. However there are areas within the fibre bundles that are not impregnated resulting in porosity at these sites. The failure seems to occur perpendicular to the fibre axis and the failure mechanism indicates a relatively strong interface.

The fibre strength is relatively unchanged at pH in the range 7 to 3 while severe reduction of fibre strength occurs at pH below 2.

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